PB84-133768

Conversion of Sewage Sludge to Oil by Hydroliquefaction

Worcester Polytechnic Inst., MA

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Jan 84

U.S. Department of Commerce
National Technical Information Service

PB84-133768

EPA-600/2-84-010
January 1984

CONVERSION OF SEWAGE SLUDGE TO OIL BY HYDROLIQUEFACTION

by

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Cooperative Agreement No. 807390010

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CINCINNATI, OHIO 45268

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-84-010		PB84 133768

4. TITLE AND SUBTITLE	5. REPORT DATE
CONVERSION OF SEWAGE SLUDGE TO OIL BY HYDROLIQUEFACTION	January 1984
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Wilmer L. Kranich	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Worcester Polytechnic Institute Worcester, MA 01609	11. CONTRACT/GRANT NO. CR 807890-01

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Atal E. Eralp, (513) 684-2621

16. ABSTRACT

A study was undertaken to determine the feasibility of converting municipal wastewater sludes into oil under hydrogen pressure. In a laboratory autoclave, raw and digested sludges were subjected to 14 MPa total pressure for 20 to 90 minutes. Aqueous suspensions were treated at about 300 °C while predried sludge suspended in an oil carrier was reacted at about 425 °C. When the predried sludge solids were suspended in an oil carrier, 50 percent of the organic content of sludge was converted into pentane-soluble oil; but significant amounts of oil were not produced under the conditions studied when the sludge solids were slurried in water. A commercial plant using the oil carrier process scheme would be complex with high capital and operating costs. Consequently, further development work on hydroliquefaction of sewage sludge is not recommended.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	34
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; It involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This study addresses the problem of ultimate disposal of sewage sludge. The method investigated is treatment of the sludge with hydrogen under pressure with the objective of converting insoluble organic material into useful liquid and gaseous fuels.

Francis T. Mayo, Director
Municipal Environmental Research
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ABSTRACT

The objective of this study was to assess the feasibility of ultimate disposal of sludge from municipal sewage treatment plants by reaction with hydrogen at high pressure and temperature. Conversion of most of the organic material to useful liquid and gaseous fuels was anticipated.

Small scale processing of sewage sludge from the Deer Island Sewage Treatment Facility in Boston was carried out in stirred batch reactors. Experiments were performed on raw settled sludge, settled sludge from within the digesters, and digested sludge as discharged to the harbor.

In some experiments the sludge was pre-dried and slurried in a carrier oil before processing with hydrogen in the presence of a nickel catalyst. In other runs the sludge was treated in water suspension as received, in the presence of a sodium carbonate catalyst.

Total conversion of organic material, and conversion to oil product was measured using a solvent extraction technique.

Conversions of up to 90% of the organic material were achieved in both the oil-slurried and water-slurried runs, but significant conversion to oils occurred only in the oil-slurried experiments (which were run at temperatures of about 400°C).

An analysis of a proposed commercial process based on pre-drying the sludge and suspending it in oil before treatment with hydrogen at high temperatures and pressures did not yield encouraging results. The high cost of drying, the complexity of the plant including auxiliary hydrogen and oxygen generation facilities, the limited yield of oil, and the high ash content of the sludge suggest that further work toward commercial development of this process not be encouraged.

This study was performed in fulfillment of Cooperative Agreement No. 807390010 between the U.S. Environmental Protection Agency and the Worcester Polytechnic Institute, covering the period April 27, 1981 to January 26, 1983.

INTRODUCTION

It is estimated that by 1985, 23,000 tons of sewage sludge (on a dry basis) will be produced daily in the United States (1). The treatment and disposal of this material presents a major challenge.

Until recently sewage sludge disposal practices were roughly distributed as follows (2): 25% incinerated; 25% landfilled; 5% lagooned or stockpiled; 15% ocean disposed; and 30% landspread. Although all of these options are obviously commonly practiced, all have serious drawbacks that make them expensive or environmentally unsuitable in some situations.

Katz, et al. (3) have reviewed various sludge management strategies. They reject incineration/pyrolysis because of economics, its limited availability and low state-of-the-art technology. Landfill or agricultural applications are economic when sites are within thirty miles. Silviculture is generally uneconomic because of larger distances. Heat-drying is economically prohibitive and produces undesirable characteristics. Composting has market limitations. Agricultural applications are also limited by the inorganic content of sewage sludge in particular areas. Sludges with an industrial waste component may, for example, contain undesirable metals which may be absorbed by plants and transmitted to agricultural products.

Niessen, et al. (4) have reviewed the incineration of sewage sludge with municipal solid wastes and have developed economics for the process (5). They suggest that co-incineration is most successful when sludge is predried from about its 15% solids to 80% solids. Special sludge dryers are available to conduct this drying step. They describe the "porcupine" dryer in detail. Incineration temperature must be high enough to avoid odors. Co-incineration faces formidable institutional and sociological hurdles, and if not properly conducted can have substantial negative environmental impact. Like the other disposal methods, it is far from an ideal or universal solution to the sludge disposal problem.

The Resource Conservation and Recovery Act, the Clean Water Act, The Marine Protection, Research and Sanctuaries Act and the Clean Air Act authorize EPA to manage municipal sludge disposal. Congressional goals for implementation of these Acts include not only protection of health and environment but also the disposal and/or utilization of sewage sludge in such a manner as to conserve natural resources. The present study has, therefore, been undertaken to investigate the possibility of converting sewage sludge into oil.

Previous work carried out in the Resource Recovery Laboratory at Worcester Polytechnic Institute has been concerned with the conversion of α-cellulose and powdered newspaper into gaseous and liquid fuels (6,7).

These materials were used to model the behavior of combustible municipal solid waste. These studies involved the hydroliquefaction/hydrogasification over nickel catalysts of cellulosic substances slurried in paraffin oil at temperatures between 350°C and 450°C and under hydrogen pressure in the range of 3×10^6 to 8×10^6 Pa. It has been shown that under such conditions up to 90% of cellulosic substances can be converted to gaseous and liquid fuels. More recently a related program has been undertaken at Worcester Polytechnic Institute to study the kinetics and mechanisms involved in the hydroliquefaction of lignite slurried in anthracene oil over cobalt-molybdenum catalyst.

The background, techniques, and experimental equipment associated with the cellulose and lignite liquefaction studies have been applied in this investigation to the hydroliquefaction and gasification of sewage sludge.

STARTING MATERIAL

Because of the special interest of EPA Region I in this project, the raw material (sludge) was taken entirely from a major Boston sewage disposal plant. The Deer Island sewage treatment plant is located near the mouth of Boston harbor in Winthrop, Massachusetts. Deer Island serves over 1.3 million people in Boston and 25 neighboring communities (8). The sewage undergoes a primary treatment consisting of screening, grit removal and settling. The primary sludge from settling tanks is further treated in digesters.

The primary function of the digesters is to break down the sludge with the aid of bacteria and other micro organisms, yielding gases and digested sludge. The digesters are run at a constant temperature of 35°C in order to speed up the anaerobic process. Methane makes up 62% of the digester gas while the other 38% is made up of carbon dioxide (9). The gas is stored and used as a source of fuel for the treatment plant and neighboring detention facility.

At the present time, the digested sludge is chlorinated and mixed with the wastewater and dumped into the harbor on the outgoing tide. An average of 334 million gallons of treated sewage is dumped into the harbor each day (8). This effluent is considered responsible for an increase in the coliform bacteria count in the surrounding waters which has an adverse effect on the nearby beaches and fishing industry. Therefore, the dumping of sludge into the ocean may be discontinued in the future. Since the treatment facility is located in an urban area, the cost of transporting the sludge to land application sites will be high and alternate methods of disposal are under consideration.

It is very difficult to obtain samples of raw or processed sludge with any degree of uniformity. In the early part of this study we had small samples shipped from Deer Island to Worcester on a weekly basis. Later, because of variation of shipped material during groups of related runs, we drove to Deer Island and obtained sufficiently large samples that they would last for a full series. This introduced its own problems in that the stored material underwent some bacterial decomposition. Each series was run in as short a time as possible.

Runs were made on three types of raw material:

1) Primary sludge - as delivered to the digesters by pipeline from the settlers.

2) Settled digested sludge - material near the bottom of the digesters.

3) Digester effluent - taken from the transfer line to harbor discharge.

In each case the lines were well flushed before the grab samples were taken. It should be noted, however, that day-to-day, seasonal, and operating variations affected the composition of all streams. During one sampling period, for example, the plant was recovering from the collapse of the cover on one tank. During another, the gas generation step was performing poorly and the production of methane was quite small. Sludge concentration and ash content could vary significantly depending on rainfall.

Accordingly the quantitative results of this study should not be generalized, but internal comparisons of the relative effects of the variables studied should be valid.

Hydroliquefaction studies were performed in two general ways (as described in more detail in later sections):

1) On as-received aqueous suspensions

2) On dried samples dispersed in an oil carrier.

The only special preparation of the as-received raw materials was to stir the contents of the storage drum to obtain as representative a sample as possible. In commercial practice the sludge would be partially dewatered and/or centrifuged, but neither Deer Island nor WPI had appropriate equipment. The results must be interpreted taking into account the process economic effect of partial mechanical dewatering.

Dried samples were prepared in two ways. The first involved direct low temperature (below 100°C) drying in a nitrogen atmosphere to avoid oxidation by air. In the second method the sludge was first dewatered in a laboratory centrifuge and the supernatant liquid discarded before drying. The difference in the results caused by the presence of the dried dissolved salts was not measurable within the limits of accuracy of the experiment. Evidently the soluble salts do not have a catalytic effect. As a result the tedious centrifuging step was discontinued.

The dried material was ground to a fine powder and slurried in carrier oil.

APPARATUS AND PROCEDURE

The principal apparatus consisted of a magnetically-stirred batch autoclave manufactured by Autoclave Engineers, Inc. Auxiliary equipment included a hydrogen-feed system, a slurry-feed device, pressure and temperature recorder-controllers, a wet-test meter for measuring the amount of off-gas, and analytical equipment for determining the composition of the liquid and gas products, and the conversion of the sludge.

The apparatus is shown schematically in Figure 1.

Oil-Carrier Runs

A slurry of dried powdered sludge dispersed in anthracene or paraffin oil was prepared in a beaker and warmed to produce a free-flowing mixture. A measured amount of catalyst was added to the reactor and the unit cover was bolted on. The reactor was heated using an electric resistance jacket to about 25°C above the desired temperature for the run.

The feed slurry was added to the injector vessel, then rapidly forced into the reactor by hydrogen pressure. Addition of hydrogen was continued until the desired initial reaction pressure was reached. With this technique it was possible to reach a stable desired reaction temperature within about two minutes following injection because the massive reactor was preheated above the desired reaction temperature. Thus the initial time for the run was closely established by avoiding long slow heatup periods often experienced in batch reactor studies.

The end point of the reaction was also closely determined by rapidly cooling the reactor using cooling water in the internal coils. By this method the temperature could be dropped several hundred degrees in about two minutes, quenching the reaction. The heating jacket was then removed and cooling continued to ambient temperature.

The reactor gases were then vented through a zinc acetate bubbler to trap hydrogen sulfide, then through a wet test meter to measure gas volume and from there to an exhaust system. Gas samples were taken several times during the venting for analysis by gas chromatography.

The slurry was analyzed by a solvent-fractionation scheme widely used in the analysis of coal-derived liquids (10). A slightly modified version of this method was used in the present study. According to this scheme, the portion of the dry sewage sludge that is soluble in pentane is termed oils (primarily paraffinic materials), and the difference between the

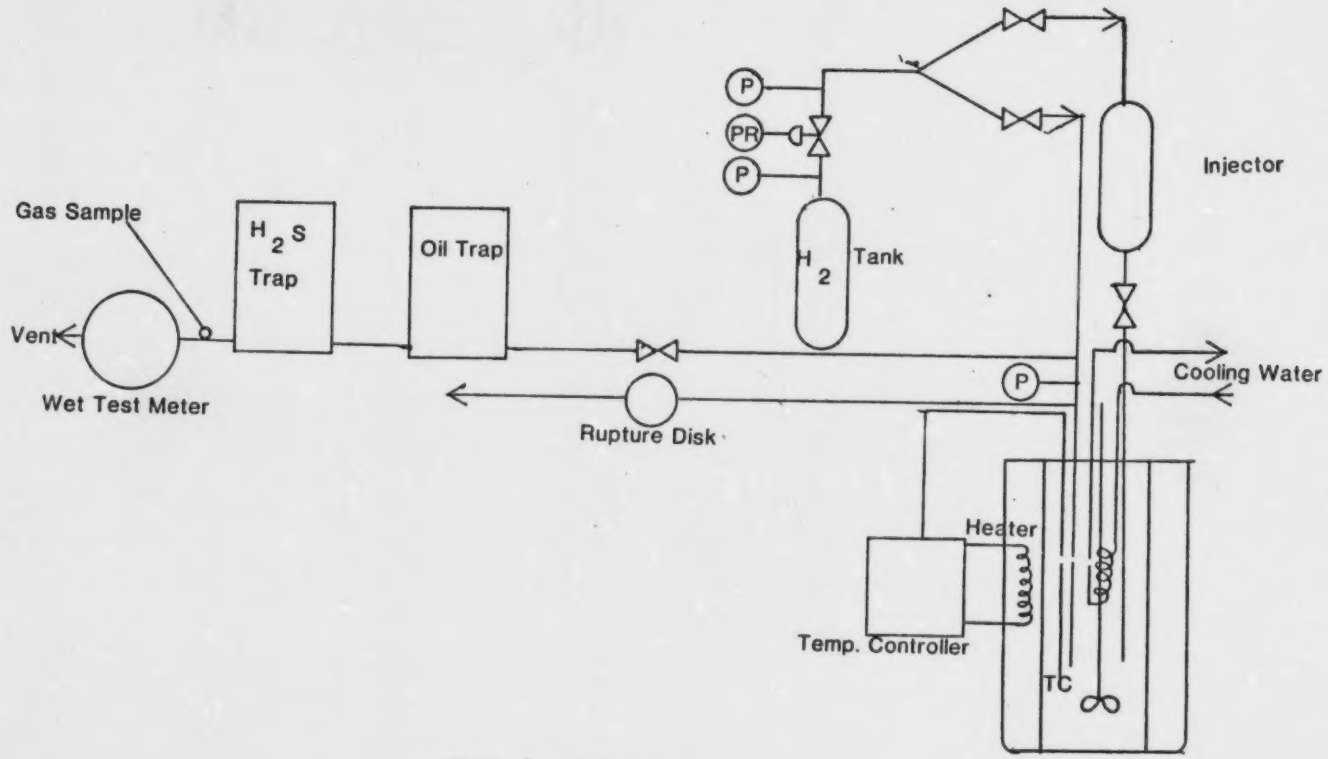

FIGURE 1 BATCH REACTOR

toluene-soluble and pentane-soluble fractions is called asphaltenes (primarily aromatic or complex compounds). (Asphaltenes are recognized as intermediate products in coal liquefaction.) Toluene-insolubles consist of convertible organic materials plus ash.

Extractions were carried out for 18 hours in a Soxhlet apparatus as follows. The material to be extracted was placed in a weighed porous thimble, inserted in a vessel, and the appropriate solvent trickled through. The extract flowed to a heated receiver from which the volatile solvent was boiled off, condensed and recirculated through the thimble. The loss in weight of the thimble after drying corresponded to the material removed by the solvent.

The amount of water in the samples was determined by xylene distillation.

Ash analyses (inorganic, non-volatile residues) were made by gradually heating a weighed sample in air to 750°C and holding until constant weight was achieved.

Water-Slurry Runs

Runs were also made on the as-received sludge. Because of the heterogeneous nature of this material, it could not be forced from the injector through the small connector tubing into the reactor. Consequently runs on this material were made with the sludge and catalyst added directly to the reactor before heating. A heat-up time of a half hour or more, resulting in an indefinite run time, could not be avoided.

It was not possible to operate with as high a partial pressure of hydrogen as in the oil carrier runs because of the vapor pressure of steam. This further limited the reaction temperatures studied to below 300°C so that the total pressure would remain below 1.4×10^7 Pa, the safe upper limit.

Water content of the slurry was determined by drying at about 100°C in a nitrogen atmosphere rather than by xylene distillation.

Otherwise the procedures were those followed for the oil-slurry runs.

Analysis of Raw Materials, Sludge and Oils

As noted previously, the sludge concentration and composition varied seasonally and with operating conditions in the plant. The key components - oils, asphaltenes, toluene-insoluble organics, and ash - were measured for each batch. Elemental analyses were obtained only for representative samples.

Representative analyses for settled digester sludge and Digester outflow are given in Tables 1 and 2; (ultimate analysis and physical properties of of the anthracene carrier oil are given in Table 3).

TABLE 1. AVERAGE ANALYSES OF TYPICAL DRY SETTLED DIGESTER SLUDGE AND FINAL OUTFLOW

Component	Settled Digester Sludge, %	Digester Outflow to Harbor %
Oils	8.6	5.3
Asphaltenes	4.0	5.1
Organic toluene-insolubles	72.4	53.2
Ash	15.0	36.4
Total	100.0	100.0

TABLE 2. ELEMENTAL ANALYSES OF TYPICAL SETTLED DIGESTER SLUDGE AND FINAL OUTFLOW (DRY ASH-FREE BASIS).

Element	Settled Digester Sludge, %	Digester Outflow to Harbor %
C	55.3	52.2
H	8.0	7.3
N	3.1	6.2
S	0.9	2.2
O	32.7	32.1
Total	100.0	100.0

TABLE 3

Anthracene oil ultimate analysis

Element	(wt. %)
C	86.85
H	10.64
N	nil
S	2.05
O (by difference)	0.46
Ash, wt. %	nil

Anthracene oil physical properties

Distillation Range	(wt. %)
0 to 210°C	0.0
0 to 235°C	0.36
0 to 270°C	1.24
0 to 315°C	5.78
0 to 355°C	25.88
Specific gravity at 38°C/16°C	0.989
Viscosity at 38°C (Saybolt Universal Seconds)	3000

RESULTS

The principal results are reported in terms of the total fractional conversion of the toluene-insoluble organic feed and the fractional conversion into oils (pentane solubles). These are calculated by the following relationships:

$$\text{Conversion to Oil, } X_O = \frac{\left(\begin{array}{l}\text{(weight of oils}\\ \text{in product slurry)}\end{array}\right) - \left(\begin{array}{l}\text{(weight of oils in sewage}\\ \text{sludge and carrier oil)}\end{array}\right)}{\left(\begin{array}{l}\text{(weight of organic toluene-insolubles in}\\ \text{sewage sludge)}\end{array}\right)} \times 100$$

$$\text{Conversion of Toluene-Insolubles, } X_{TI} = \frac{\left(\begin{array}{l}\text{(weight of organic}\\ \text{toluene-insolubles -}\\ \text{in sewage sludge)}\end{array}\right) - \left(\begin{array}{l}\text{(weight of organic}\\ \text{toluene-insolubles}\\ \text{in product slurry)}\end{array}\right)}{\left(\begin{array}{l}\text{(weight of organic toluene-insolubles -}\\ \text{in sewage sludge)}\end{array}\right)} \times 100$$

Thus X_O represents the net oil yield per unit insoluble organic material in sewage sludge and X_{TI} represents the conversion of the insoluble organic material in sewage sludge to all liquid and gaseous products.

Dried Settled Digester Sludge and Dried Final Effluent

The first set of data was taken on dried sludge as settled in the digester or as sent to the ocean. In these experiments the carrier was a low volatility paraffin oil completely soluble in pentane (i.e. containing no asphaltenes).

Figure 2 shows the variation of total conversion with reaction time for the settled sludge in the digester, and Figure 3 shows the same variables for the final discharge. In both cases the results varied very little after about 30 minutes of reaction time at the desired temperature. Direct quantitative comparison of the two curves is not feasible because of differences in operating conditions, but it may be concluded that 80% or more of the toluene-insoluble organic material is converted in both cases.

Conversion to oil, X_O, was also calculated by the given formula as a function of reaction time for both feeds and plotted in Figures 4 and 5. In both cases similar, positive oil yields are obtained in relatively short reaction periods. However, in longer reaction periods oil conversion

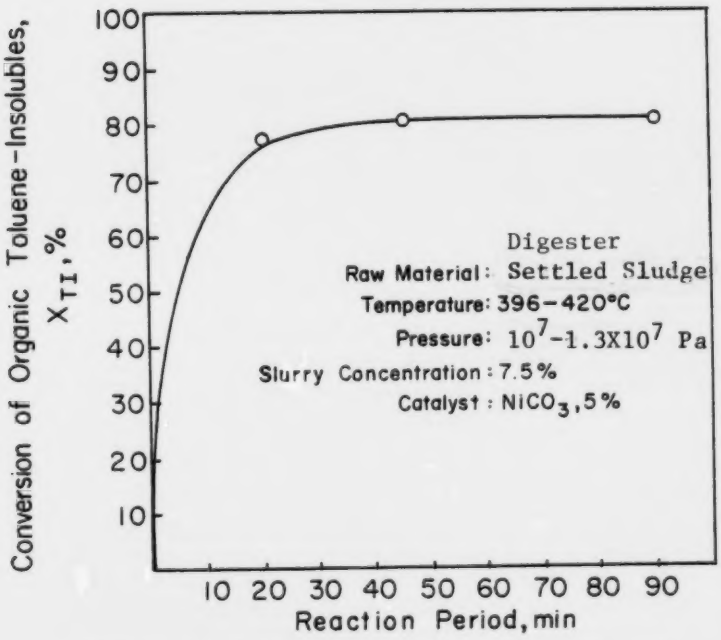

Figure 2 Effect of Reaction Period on Conversion of Organic Toluene-Insolubles

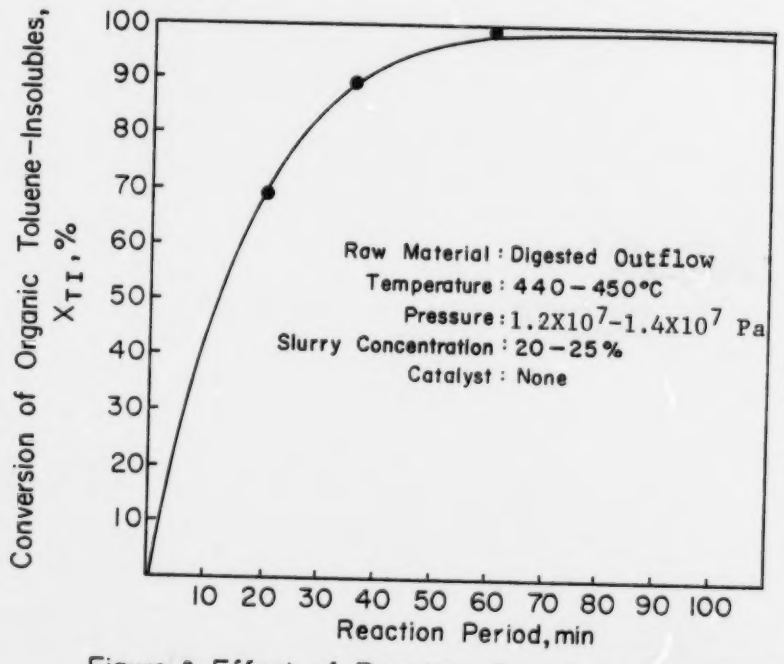

Figure 3 Effect of Reaction Period on Conversion of Organic Toluene - Insolubles

apparently falls to negative values. This is as a result of increased gas production at the expense of oil production from toluene-insolubles and from the cracking of the carrier oil into gaseous products. The following rough mechanism for the hydroliquefaction-hydrogasification of sewage sludge is consistent with these results.

$$\left[\begin{array}{c}\text{convertible}\\ \text{organic matter}\end{array}\right] \rightarrow \left[\begin{array}{c}\text{intermediates}\\ \text{asphaltenes, etc}\end{array}\right] \rightarrow \text{oils} \rightarrow \text{gases}$$

This mechanism is the same as that proposed for the hydroliquefaction/hydrogasification of cellulosic substances (7). If this mechanism is correct, it can be expected that optimum conditions exist under which oil yield is maximized. For our experiments this would occur at a reaction time less than 20 minutes.

The product gas has been found to contain H_2, CO_2 and C_1 to C_4 hydrocarbons. The major source of CO_2 is probably the cellulosic material in sewage sludge and the hydrocarbons probably result from the cracking of both carrier and product oils.

The effect of nickel carbonate catalyst can be more specifically observed as a single variable by comparison of two experiments which were carried out on settled sewage sludge under the following similar conditions:

$NiCO_3$ catalyst conc., %	0	5
Slurry concentration, %	25	20
Temperature, °C	420	420
Pressure, 10^7 Pa	1.2	1.0
Reaction time, minutes	20	20
X_{TI}	93.4	85.2
X_o	63.3	57.7

Addition of a nickel carbonate catalyst seems to have had no beneficial effect on either the conversion to oil or the total conversion of toluene-insoluble organic material. This may be attributed to the catalytic activity of the relatively high amount of inorganic material in sewage sludge. Additional nickel catalyst may not significantly increase reaction rate. Alternatively, of course, it may be interpreted that nickel does not function as a hydrogenation catalyst under these conditions.

In any case both the overall conversion and the conversion to oil are sufficiently encouraging to suggest that a preliminary process evaluation is worthwhile.

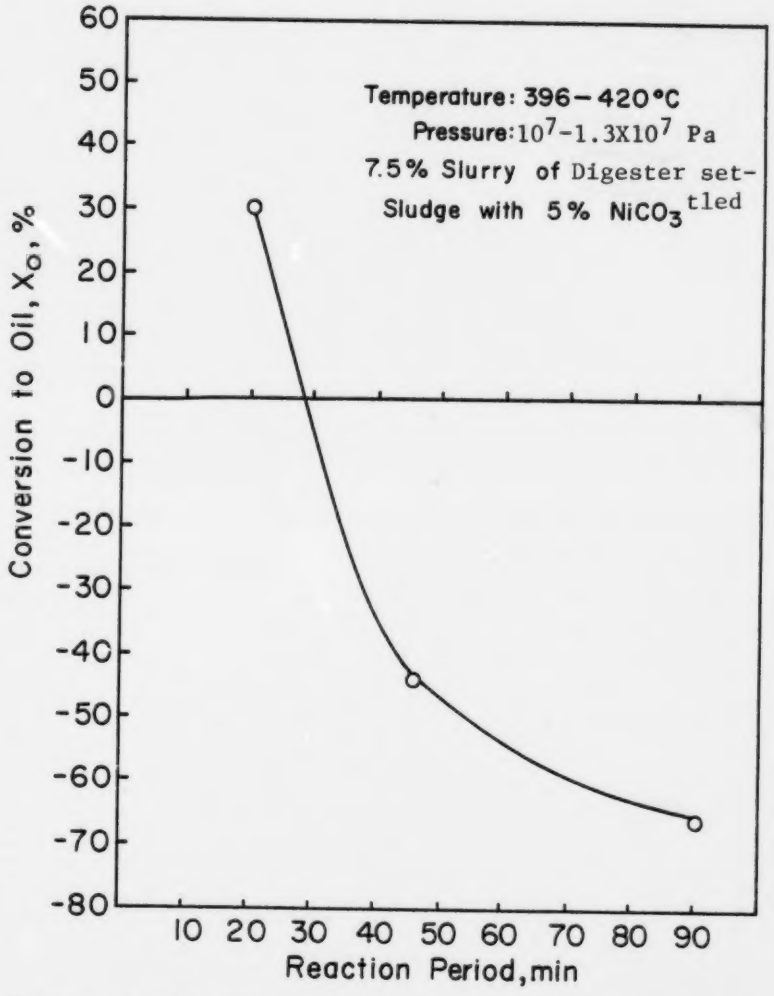

Figure 4 Effect of Reaction Period on Conversion to Oil

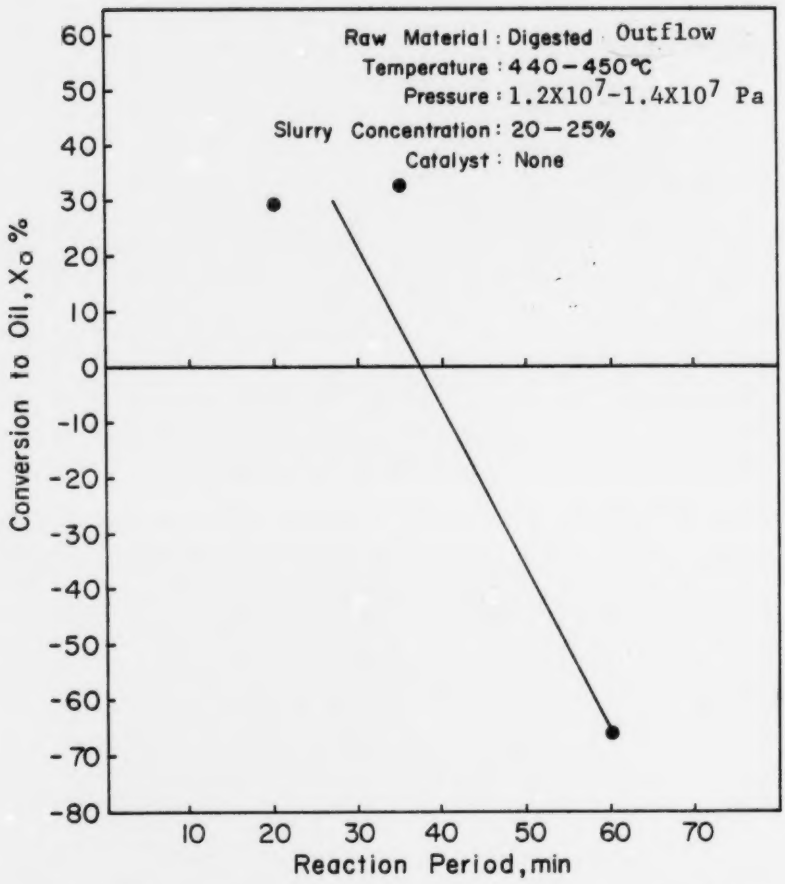

Figure 5 Effect of Reaction Period on Conversion to Oil

Dried Raw Sludge

If a practical sewage treatment process evolved from this study, it is more likely that it would be applied to the raw primary sludge rather than to settled sludge in a digester or the effluent from the digester. Anaerobic digestion has as its objective the production of a fuel gas from the same constituents which are used to produce fuel liquid in the process under investigation. Unless the new treatment were to be used as an addition to an existing plant, it seems unlikely that a two-step process (digestion plus liquefaction) would prove advantageous.

Accordingly a series of runs was made on dried raw sludge slurried in oil. This sludge was the feed to the Deer Island digesters. Since it seemed unlikely that a recirculating carrier oil in a continuous plant would have purely paraffinic characteristics, it was decided to use "anthracene" oil as carrier. The analysis was presented in an earlier section. Although this material is termed an anthracene oil, it is much less aromatic than the usual material so classified. Thus, it is a reasonable simulant for a steady-state recycle oil.

Several runs were made over a short range of temperatures (410-440°C) and reaction times (10-20 minutes), using the procedure described earlier for oil-slurries. All runs were made with 5% nickel carbonate as catalyst and at a total initial pressure of 8.3×10^6 Pa.

Results are summarized in Table 4. Because the range of variables studied is small and the analytical uncertainties are significant, the results are best interpreted on an average basis.

Over the range of temperature and reaction time studied, the conversion of dried raw sludge slurried in anthracene oil is 45±11%.

Extraction analyses are carried out on the sludge mixed with the carrier oil; pre-separation is not feasible. The analyses must therefore be corrected for the oils and asphaltenes which come from the anthracene oil.

This correction is not straightforward because the hydrogenation process converts some of the carrier oil (e.g. from "oils" to "gases"). An attempt was made to determine the appropriate corrections by a series of blank runs made with carrier oil, catalyst and hydrogen in the absence of sludge. The results are shown in Table 5. Under these reaction conditions, about 3-1/2% of the oil in the carrier was lost, presumably by conversion to gas (or possibly to insoluble residue). If this lost amount is added as a correction to the oil actually observed in the runs with sludge, the calculated oil produced is greater than the total amount of dry sludge converted - an impossible result. It is concluded that the carrier oil behaves differently alone than in the presence of sludge. Since the amount of carrier oil is more than ten times the amount of sludge, uncertainty in the attempted correction is too large to permit its application.

Conversions of dried sludge slurried in oil may not be economically attractive in view of the large cost of drying. Furthermore the high ash content of the dried sludge indicates a relatively low overall fuel potential for sewage sludge.

It seems likely that the smaller the amount of pre-processi equired, the greater is the likelihood that an economically feasible proce can be achieved. Accordingly the final series of runs was directed toward direct hydroliquefaction of the wet sludge as received.

A further potential cost saving of a water-slurry process is the possible internal generation of some or all of the hydrogen by the water gas and shift reactions. If, for example, cellulose monomer is taken as the model for sewage, the water gas reaction with partial shift would ideally produce hydrogen as follows:

$$C_6H_{10}O_5 + 2H_2O \rightarrow 5CO + 1CO_2 + 7H_2$$

Ideally the H_2 would react with another cellulose monomer to produce hexane (C_6H_{14})

$$C_6H_{10}O_5 + 7H_2 \rightarrow C_6H_{14} + 5\ H_2O$$

Obviously it is not expected that reactions would proceed as shown under the experimental conditions experienced here. They are presented only as an idealized goal.

Since it seemed likely that insoluble catalysts would be less effective in promoting hydrogenation in an aqueous slurry, Na_2CO_3 was added as a soluble catalyst. This material has been used in hydrotreating of similar materials such as wood wastes.

As noted in the Procedure section, because of the vapor pressure of water and the limitations of the autoclave it was necessary to operate at much lower temperatures than in the oil slurry runs. With an initial hydrogen pressure of 3.5×10^6Pa, reaction temperatures were limited to about 300°C. Under these conditions generation of significant amounts of hydrogen by water gas and shift reactions is unlikely.

Because of the large amount of water present and the difficulties of accurately measuring the products of the solvent extractions, determination of conversion to oils was very uncertain.

The results shown in Table 6 indicated that up to 90% of the toluene-insoluble organic materials in the sludge was converted to liquid and gaseous products. This occurred whether or not hydrogen was introduced above one atmosphere or whether or not catalysts were added.

Apparent conversion to oils was extremely variable and seemed not to depend on the addition of hydrogen or catalyst. Conversion to oil was generally less than 20% and in many cases the oil and asphaltenes measured in the product were less than those in the sludge feed.

TABLE 4. CONVERSION OF DRIED SLUDGE IN ANTHRACENE OIL SLURRY

Run	2	3	5
Initial H_2 pressure, 10^6Pa	8.3	8.3	8.3
Temperature, °C	425	440	425
Catalyst	$NiCO_3$	$NiCO_3$	$NiCO_3$
Reaction time, min.	20	20	10
INPUT, gram			
Sludge			
Ash	3.17	3.52	3.96
Oil	1.53	1.73	1.94
Pentane-insoluble organics	5.42	5.84	6.87
Anthracene oil			
Oil	111.60	101.83	115.27
Water	2.25	1.23	1.22
Pentane-insoluble organics	0.34	0.31	0.35
OUTPUT			
Oil	113.49	103.99	116.31
Pentane-insoluble organics	2.68	3.00	4.78
Conversion of pentane-insoluble organics Total, %	53	51	34
To oils (corrected for "blank" - see Table 5), %	64	57	35

TABLE 5. "BLANK" RUNS ON ANTHRACENE OIL WITH CATALYST AND HYDROGEN BUT NO SLUDGE

Run	BL-1	BL-2	BL-3	BL-4
Temperature, °C	425	425	425	425
Initial H_2 pressure, 10^6 Pa	8.3	8.3	8.3	8.3
Reaction time, min	20	20	15	30
Feed				
Oils	98.0	98.6	98.7	98.9
H_2O	1.7	1.1	1.0	0.8
Liquid product				
Oils	96.4	95.5	94.2	95.3
H_2O	0.6	1.0	1.0	0.6
Loss of oils, %	1.6	3.1	4.6	3.6

TABLE 6. CONVERSION OF RAW SLUDGE IN WATER SLURRY.

Run	B-2	B-3	B-4	B-5	A-4	A-6	A-8	A-9
Temperature, °C	285	285	285	285	295	295	295	295
Time at temp, min.	15	15	15	15	20	20	20	20
Initial H_2 pressure, 10^6Pa	2.9	0	2.9	0	0	0	3.5	3.5
Catalyst	Na_2CO_3	Na_2CO_3	None	None	None	Na_2CO_3	Na_2MoO_4	$NiCO_3$
Conversion of dry pentane-insoluble organics								
Total, %	40	86	88	90	76	93	99	79
To oils, % (apparent)	14	11	<0	<0	<0	27	1	<0

Runs made with nickel carbonate (insoluble) and sodium molybdate (water soluble) as catalysts did not show any significant difference in result.

Conversion of toluene-insoluble organics in the feed seems to result primarily from reaction with steam at high temperatures rather than from hydrogenation. The products are gases and water-soluble liquids rather than oils.

Although the range of possible operating conditions using wet sludge as feed is certainly not exhausted and the consistency of results is limited, there is little evidence to encourage further experimentation.

PROCESS ANALYSIS

Since no significant amount of oil was produced in the experiments on water slurries of sewage sludge, consideration of a commercial scale process was confined to the oil-slurry system.

There is no apparent advantage in a large new sewage treatment plant to a combination of digestion and hydroliquefaction. Interest is therefore confined to a process directly treating raw sewage sludge. A conceptual flow sheet is given in Figures 6 and 7.

Incoming sewage is given a preliminary treatment as at present. Brief aeration in an open tank produces a floating organic scum which is skimmed and added back to the recovered sludge, and coarse inorganic grit which is discarded.

The settled organic sludge contains about 95% water. This is partially de-watered in a continuous solid bowl centrifuge, then dried in a steam heated dryer. The dried product is pulverized, then mixed with recycle oil.

The slurry is pumped to the first of two continuous stirred tank reactors (CSTR) operated at 425°C and 1.4×10^7 Pa. Overflow slurry passes to the second CSTR. From there the slurry is flashed and the condensed vapor is removed as oil product.

The remaining slurry is centrifuged in a continuous solid bowl unit and the liquid is recycled as carrier oil.

Solids are washed with a part of the light oil product. This solvent is recovered by vaporization and condensation. The residual washed oil is returned as part of the recycle and the solids pass to the hydrogen plant.

Here the unconverted carbonaceous residue is burned from the ash with limited oxygen (coming from a separate oxygen plant) to produce carbon monoxide and hydrogen. The carbon monoxide is oxidized with steam in the following shift converter, producing more hydrogen.

After gas purification to remove CO_2, H_2S and light hydrocarbons, the hydrogen is fed to the second CSTR. Gases leaving this reactor are cooled to liquefy a portion of the oil product, then passed to the first CSTR. Again, the off-gases are cooled to condense oil, then further cooled to condense light liquid hydrocarbons. The remaining gases pass through the purification system and are then recycled.

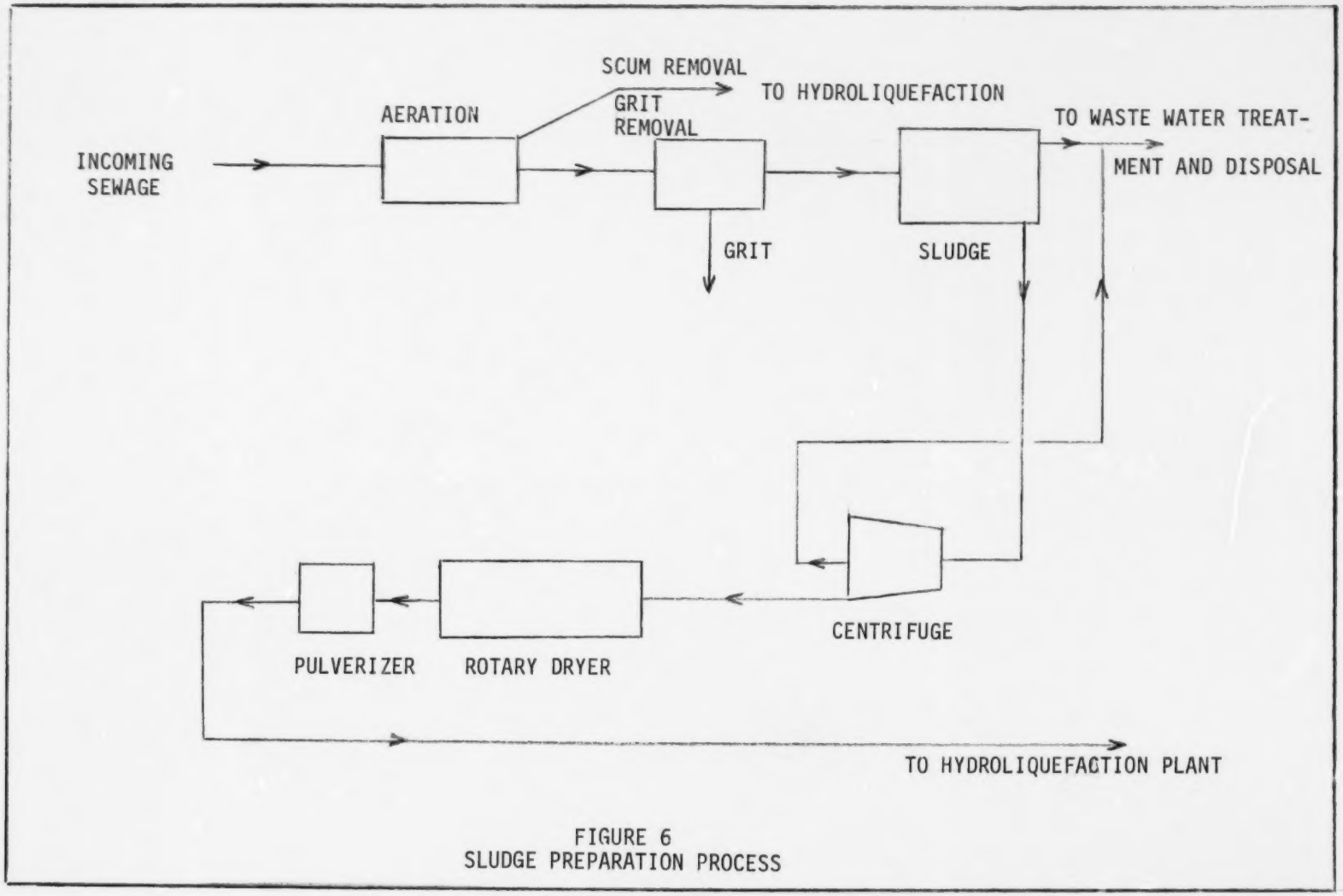

FIGURE 6
SLUDGE PREPARATION PROCESS

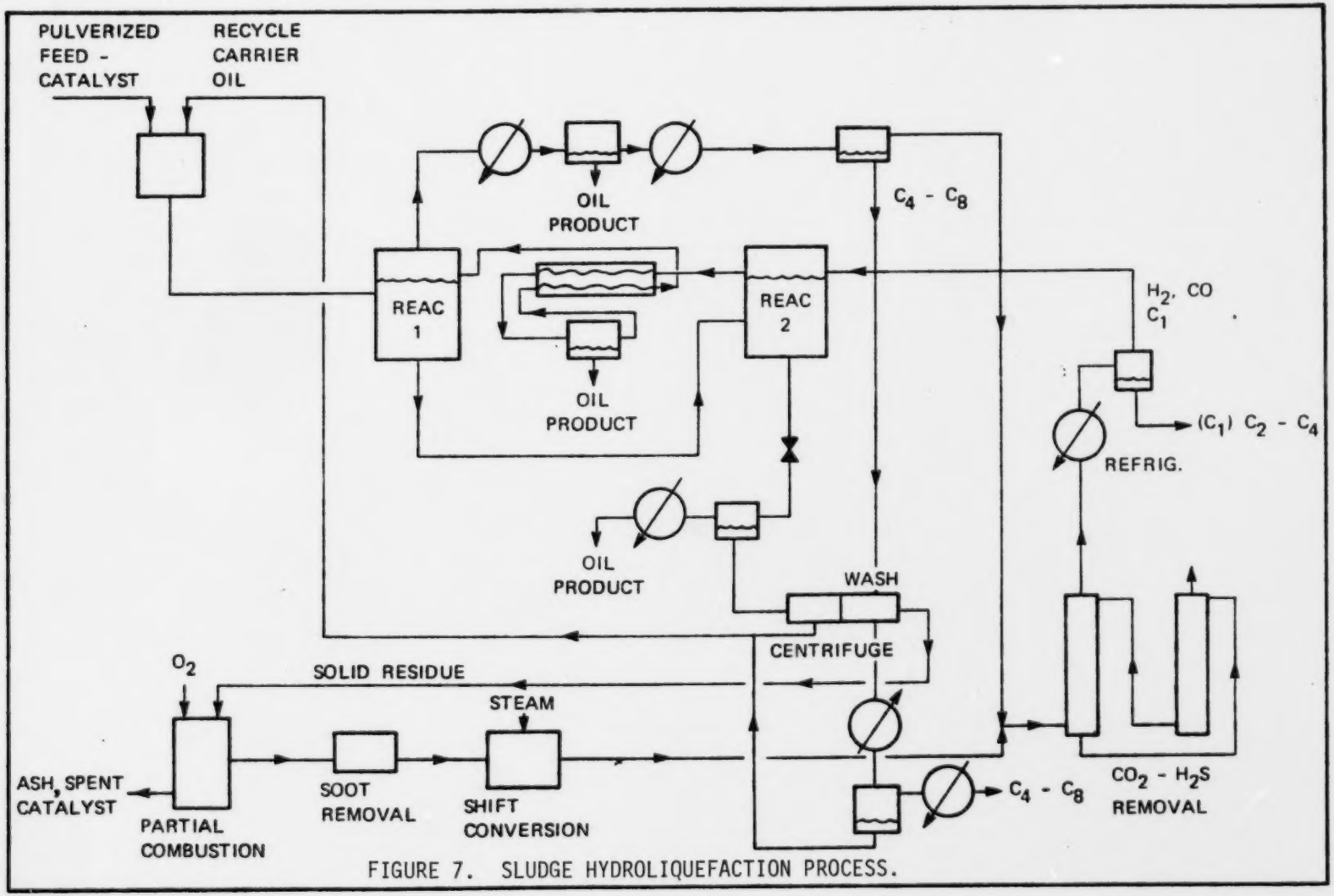

FIGURE 7. SLUDGE HYDROLIQUEFACTION PROCESS.

The degree of conversion in the reactors is controlled so that partial combustion of the remaining organics will produce the hydrogen needed in the process.

A portion of the oil and gas product is used as fuel for producing steam to dry the sludge and operate the shift converter.

As is obvious from the conceptual flow sheet, the process based on the technology of this study is quite complex and contains many sections which would require much further investigation before a demonstration plant could be built or costs determined with confidence.

The need to dewater and dry the sludge is a serious drawback. The dewatering step is itself costly. Our laboratory tests on filtration have not been encouraging. Filters clog quickly with the miscellaneous content of the sludge. The solid bowl centrifuge which is used in the proposed flow sheet is an expensive, rather delicate machine, which uses considerable power and cannot recover any of this energy. Niessen (5) has shown that a special steam dryer is required which has a high fuel requirement and little opportunity for energy recovery.

The use of two CSTRs is suggested by the successive nature of the reactions. At an optimum residence time the oil yield is maximized. Furthermore the removal of light oil product between stages reduces oil losses from breakdown into gases. However, the multiple high pressure reactors and associated heat exchange and separation equipment represent a major investment.

Recovery of unconverted solids from recycle oil in a centrifuge would require extensive experimental verification. This step has proved troublesome in coal liquefaction plants.

The hydrogen generating facility is also a major investment and operating cost, particularly since it must also contain an oxygen plant. Gas purification steps add considerably to the cost.

Nothing is known of the nature of the oil product since it is recovered in our studies only as a portion of the anthracene carrier oil. In practice this would be a recycled portion of the product, which after many cycles would reach an unknown steady-state composition. In a pilot plant operation on hydroliquefaction of lignite at Grand Forks Energy Technology Center (DOE), the steady state recycle oil evolved into a very viscous liquid which was extremely difficult to process.

A major drawback is the fact that the sewage sludge contains more than 30% ash on a dry basis. This seriously reduces the potential oil recovery per ton of dry sludge.

Although this project has demonstrated that oil can be made by hydroliquefaction of dried sewage sludge in an oil carrier, the cost and complexity of the necessary production plant are not encouraging to further development.

CONCLUSIONS

1 Raw sewage sludge and sludge settled in the digesters can be largely converted to liquid and gaseous products by heating the water slurry to about 300°C under its vapor pressure. Conversion of up to 90% of the toluene-insoluble organics can be achieved with or without added hydrogen.

Sodium carbonate, sodium molybdate or nickel carbonate catalyst do not significantly alter the result.

2 Significant amounts of oils were not produced from the water-slurried sludge under any of the conditions studied.

3 If raw or settled digester sludge, or the final effluent sludge from the digesters is dried, ground and slurried in a carrier oil, up to 90% of the toluene-insoluble organic content can be converted in 20 minutes in the presence of hydrogen at a total initial pressure of 8.3×10^6Pa and about 425°C.

4 Under these conditions, up to 50% of the material so converted may be recovered as oils or asphaltenes.

5 The great complexity and high projected investment and operating costs of a commercial plant based on the results of these experiments do not encourage further development work on hydroliquefaction of sewage sludge.

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